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Surface-enhanced, multi-dimensional attenuated total reflectance spectroscopy

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ABSTRACT

Ultrafast two-dimensional infrared spectroscopy (2D IR) spectroscopy is performed in attenuated total reflectance (ATR) geometry with the Kretschmann configuration in order to measure femtosecond to picosecond dynamics of self-assembled monolayers on gold-coated solid-liquid interfaces. In the monolayers low-absorbing ($<200 \text{ M}^{-1} \text{ cm}^{-1}$) nitrile functional groups are used as local vibrational probes to monitor vibrational relaxation and spectral diffusion in dependence of different environments of the nitrile group. By comparing spectral diffusion dynamics of the vibrational probe in bulk solution and in the monolayer we find that the dynamics are slowed down by more than a factor of 20 upon immobilization of the sample. Moreover, spectral diffusion dynamics are affected by the local environment within the monolayers as evidenced by 2D ATR IR experiments on mixed monolayers with different aliphatic and aromatic co-adsorbates. The results are interpreted in terms of absent excitation energy-transfer as well as solvation dynamics around the nitrile vibrational probe. Our results demonstrate that 2D ATR IR spectroscopy offers the possibility to obtain ultrafast dynamics from sub-monolayer coverages of even low-absorbing vibrational probes such as nitrile functional groups.

Keywords: 2D ATR IR spectroscopy, total internal reflection, self-assembled monolayers, interfaces, nitrile, gold nanoparticles, spectral diffusion, excitation energy transfer, surface-enhanced IR spectroscopy

1. INTRODUCTION

Interfaces between solids and liquids play key-roles in chemistry and physics. For instance heterogeneous catalysis is widely used in industrial processes but a detailed understanding of structure and dynamics at the corresponding interfaces is challenging.^{1,2} Recently, additional interest regarding interfaces has been fuelled by processes such as heterogeneous photo-catalysis or hydrogen-production with nanostructured materials or molecular monolayers.^{3–6} These are expected to contribute to advanced developments in renewable energy production. As such, it is highly desirable to gain deeper insight into physico-chemical processes at solid-liquid interfaces. Particular questions are based on why molecules behave differently at interfaces compared to in bulk solution, how molecules interact with each other at interfaces and with the surface or what are the mechanisms that contribute to inter- and intra-molecular dynamics.^{6–10}

Ultrafast spectroscopy has started to tackle questions similar to the ones mentioned above by the development of different strategies for the resolution of time-domain signals from interfaces.^{6,9,11–13} A promising approach in this direction is to directly transfer knowledge from elaborated time-resolved spectroscopic techniques for bulk solution systems to methods which allow the resolution of dynamics that occur at interfaces. For instance, ultrafast, multi-dimensional infrared (IR) spectroscopy is nowadays a well-established technique, specifically suitable for the resolution of intermolecular dynamics.¹⁴ Recently, it has become possible to transfer this concept to surface-specific methods such as sum-frequency generation (SFG) spectroscopy.^{15,16} SFG spectroscopy exploits different combinations of infrared (IR) and visible (Vis) laser beams to generate a nonlinear signal which originates exclusively from sample regions that lack inversion symmetry.¹⁷ However, being a method of even orders in nonlinear susceptibility (χ^2 , χ^4 , etc.), signals from SFG spectroscopy are inherently weak. In addition, when conducted as a multi-dimensional technique, SFG requires phase-stability in the visible spectral region which is experimentally challenging.

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In this context, we have recently introduced a new method for ultrafast surface spectroscopy, namely two-dimensional attenuated total reflectance (2D ATR) IR spectroscopy (Figure 1, for a detailed description of the nonlinear experiment please see the Materials and methods section).^{18,19} ATR spectroscopy is based on the reflecting properties of interfaces between materials of different refractive indices when certain experimental conditions are fulfilled. If this is the case, then light waves from a medium of high refractive index impinging onto the interface generate an evanescent field at the interface. This evanescent field decays sharply in distance from the interface and thus penetrates a very small range (sub micrometer) into the lower-refractive index material. ATR spectroscopy is usually based on odd orders of (non-)linear susceptibility (χ^1 , χ^3 , etc.) and has been widely used to obtain spectroscopic information from a variety of samples, including self-assembled organic monolayers (MLs)²⁰, biological samples²¹ or intermediates at electrochemical surfaces²². As such, ATR spectroscopy is a method that provides surface-sensitivity and comparatively high signal magnitudes along with a direct comparability between linear and nonlinear spectroscopic results.

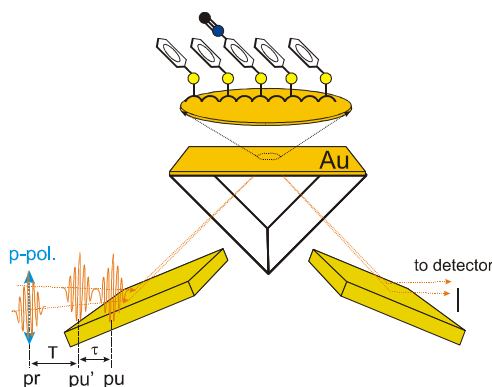


Figure 1. Experimental configuration of 2D ATR IR spectroscopy in pump probe geometry. Two collinear, coherent, femtosecond pump (pu/pu') and a probe pulse (pr) excite and interrogate the dynamics of organic monolayers (MLs) and mixed monolayers (MMLs). The MLs and MMLs are (partly) equipped with a local vibrational probe, i.e. the asymmetric stretch vibration of the nitrile group (CN). The polarization of the three pulses is indicated in case of the probe pulse.

We have recently used ultrafast 2D ATR IR spectroscopy for the investigation of femto- to picosecond dynamics of carbon monoxide and organic MLs on different metallic thin films (Figure 1).^{18,19} Here, we explore the capability of the method further by providing evidence that 2D ATR IR spectroscopy can be used to study ultrafast dynamics of samples with intrinsically low IR extinction coefficients ($< 200 \text{ M}^{-1} \text{ cm}^{-1}$) at substantial sub-ML coverage. In particular, we study MLs and mixed MLs (MMLs) of organic nitrile (CN) stretch vibrations covalently attached to thin films of gold (Au). CN functional groups obtain prominent interest in nonlinear spectroscopy since they exhibit distinct sensitivity to electrostatic environments as well as chemical interactions such as hydrogen-bonding interaction. For these reasons CN groups have been used intensively to study dynamics of electrostatics in proteins²³, chemical exchange²⁴, or electrochemistry²².

The results presented here indicate that ultrafast dynamics of spectral diffusion in ML samples of organic nitriles experience drastic differences between bulk solution samples and the MLs. Moreover, the signals are particularly sensitive to environmental changes as demonstrated in different MMLs which are designed to better expose the CN groups of the MLs to environmental interaction. Using the approach of MMLs, we additionally demonstrate that 2D ATR IR spectroscopy can be applied to study interfacial dynamics of functional groups with significant sub-ML coverage of the probe of interest.

2. EXPERIMENTAL METHODS

Ultrafast 2D IR spectroscopy is a third-order, nonlinear method which is in analogy to transient absorption spectroscopy.¹⁴ A major difference between the two methods, however, is that spectral resolution of pump *and* probe axes in 2D IR spectroscopy allow for a direct correlation between pump-probe signals for distinct pump frequencies on an ultrafast timescale. As such, 2D IR spectroscopy has its strength in yielding two-dimensional frequency-frequency

correlation diagrams (2D spectra) in dependence of a pump-probe relaxation time. Many useful information can be extracted from such diagrams which are not straightforward to be obtained by methods with only a single spectra axis. Examples of such information are for instance spectral diffusion²⁵, chemical interaction and exchange²⁶, energy-transfer²⁷ or vibrational coupling²⁸.

Laser Setup

Figure 2 shows a schematic depiction of 2D IR spectroscopy in ATR geometry and in pump-probe configuration. Spectrally tuneable ($1000 - 4000 \text{ cm}^{-1}$) pump and probe pulses are derived from a single optical parametric amplifier (OPA) and spatially separated by a BaF_2 wedge. The major portion ($> 90\%$) of the OPA output is used in the pump beam and the other fraction as probe and reference beams. The polarization of pump and probe beams can be controlled separately by use of waveplates and wire-grid polarizers. In order to derive the frequency axis of the pump excitation in the 2D spectra, two phase-coherent pump-pulses (pu/pu', Fig. 1) are necessary which need to be successively delayed with respect to each other for sampling the free-induction decay (FID) of a vibrational coherence in time (MCT signal in Fig. 2).²⁹ In brief, the first pulse generates a coherence between adjacent vibrational levels and the second pump pulse interferes with this coherence to generate population states or even higher-order coherences.¹⁴ In the pump-probe configuration of 2D IR spectroscopy which is employed here, the coherent pump pulses are derived from a Mach-Zehnder interferometer and exit the interferometer collinearly in a single beam.²⁹ Using a pyro-electric detector, the phase of the pump pulses can be directly determined from a corresponding interferogram (Fig. 2). Behind the interferometer, the pump and probe beams are focused on the reflecting plane of a single-reflection CaF_2 ATR element. In order to derive the second (probe) frequency axis in the 2D spectra, the probe beam is spectrally resolved in a conventional MCT-array consisting of 32 pixels. Finally, an additional delay between the second pump pulse and the probe pulse allows the sampling of the dynamics of 2D IR spectra during the population time (T) from which detailed dynamics of the sample can be extracted.

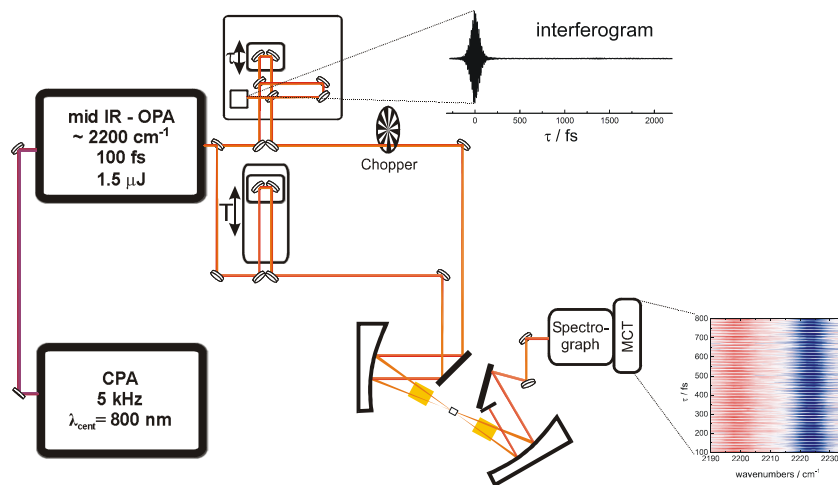


Figure 2. Ultrafast 2D ATR IR spectroscopy in pump-probe geometry and in ATR configuration (see also Figure 1). For details, see the main text.

Sample Preparation

Details about the sample preparation have been introduced previously.¹⁸ In brief, self-assembled monolayers (MLs) are generated on Au-coated CaF_2 prisms using standard procedures.³⁰ Thin (nanometer) layers of Au are sputtered onto CaF_2 prisms which are then incubated with strongly diluted solutions (1 mM) of para-Mercaptobenzonitrile (abbreviated as PhCN in the following) for 12 h, rinsed with ethanol and water and dried in a stream of nitrogen.

3. RESULTS AND DISCUSSION

2D IR spectra of PhCN under different conditions and for two representative population waiting times are shown in Figure 3. All spectra show ground-state bleach (GSB, blue) as well as excited state absorption (ESA, red) signals at about 2225 cm^{-1} and 2200 cm^{-1} , respectively. These values are typical for CN stretch vibrations in aromatic molecules.^{23,24} We note that in all cases the decay of the signals takes place with a time constant of about 8 ps which means that vibrational relaxation does not depend on the sample immobilization. Fig. 3 (a) and (b) show 2D IR spectra acquired in transmission geometry for PhCN dissolved in bulk diethylether (DEE, 30 mM). Monomeric sample conditions have been verified for the bulk solution phase experiments by means of concentration-dependent NMR experiments which showed no variations in chemical shifts and peak-widths over the investigated concentration range. White lines represent center line slopes (CLS)²⁵ fitted to GSB signals. Determination of CLS values at different population waiting times allow for quantification of inhomogeneous broadening and spectral diffusion.²⁵ At initial delays (0.15 ps, (a)) the CLS is an almost horizontal line (~ 0.1) which indicates a largely homogeneously broadened lineshape. Later delays (13 ps, (b)) yield CLS values close to zero which indicates that no long-lived heterogeneity exists in the bulk solution system and that spectral diffusion is complete on a timescale of a few picoseconds.

Significantly different behaviour is observed for PhCN immobilized on 1 nm thin Au layers on CaF_2 prisms measured in ATR configuration which are shown as DEE-incubated (Figs. 3 (c)/(d)). Here, at early waiting times (0.15 ps) GSB and ESA signals are strongly elongated in the direction of the diagonal of the 2D plots. Fitted CLS initial values (~ 0.7 at 0.15 ps, (c)) evolve within a few tens of picoseconds to about 0.4 (d). Slightly different behaviour is observed for the bare ML (Fig. 3 (e) and (f)), *i.e.* without any solvent measured in a stream of nitrogen. Here, initially CLSs exhibits values of ~ 0.6 which later evolve to ~ 0.45 . Comparison between bulk solution and ML data thus indicates that the distribution of transition frequencies is strongly influenced upon immobilization and that spectral diffusion is significantly slowed down. The alteration of the transition frequency distribution is further supported by an increase in vibrational bandwidth of the CN GSB signal from bulk DEE ($\sim 7\text{ cm}^{-1}$) to the MLs ($\sim 12\text{ cm}^{-1}$).

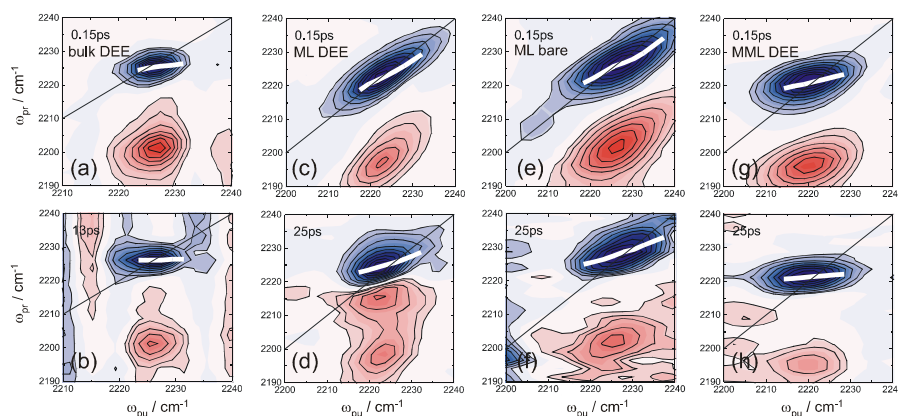


Figure 3. Exemplary 2D spectra from PhCN under different conditions for two representative population waiting times. (a) and (b) show PhCN in bulk DEE (30 mM) measured in a standard transmission geometry setup. (c) and (d) show MLs of PhCN on 1 nm Au coated CaF_2 prisms in ATR geometry incubated with DEE. (e) and (f) show MMLs of Ph-PhCN on 1 nm Au coated CaF_2 prisms in ATR geometry incubated with DEE. Note that signals are normalized to maximum GSB intensity in all cases independently to facilitate comparison.

Finally, Fig. 3 (g) and (h) show 2D ATR IR spectra of MMLs of PhCN co-adsorbed with thiophenol (Ph) on 1 nm Au on CaF_2 in a ratio of 5:1 (Ph-PhCN) and incubated with DEE. That means that only one out of six adsorbed molecules in the ML is equipped with a CN vibrational probe. Here, CLS values are initially at about 0.3 and evolve to ~ 0.1 at later stages. Hence, reduction of the surface concentration of functional groups reduces sample heterogeneity.

A detailed analysis of spectral diffusion on the basis of CLS values at a series of delays is reported in Figure 4. Experimental data are represented by open symbols while solid lines represent single exponential fits to the data. Exponential fits were conducted using a single exponential function which converges to zero (*i.e.* $CLS(T) = A \exp[-T/\tau_{SD}]$). In essence, spectral diffusion of the bulk solution sample takes place with a very low amplitude factor (0.1) time constant of about 2.3 ps (blue) while much slower dynamics are observed for the ML sample. In case of PhCN MLs incubated with DEE (red), a much higher amplitude (~ 0.7) is observed which decays with time constant of about 42 ps. The decay time constant value increases about a factor of two (80 ps) when the bare PhCN ML is considered (magenta), however, with a slightly lower amplitude (~ 0.6). Thus, heterogeneity of the CN stretch transition frequency distribution is significantly increased upon adsorption and spectral diffusion of the CN group is slowed down by at least a factor of twenty upon immobilization of the molecules. This deceleration is thus much larger than reported previously for aliphatic azide groups in MLs under similar conditions¹⁸. The experiments also show that the immersion of the MLs with solvent fastens the spectral diffusion. This indicates that structural fluctuations within the ML are facilitated in solvated environments. These structural fluctuations must originate from inter-molecular interactions such as π -stacking within the ML due to the inherent rigidity of the PhCN molecule not allowing for rotations of bonds or functional groups.

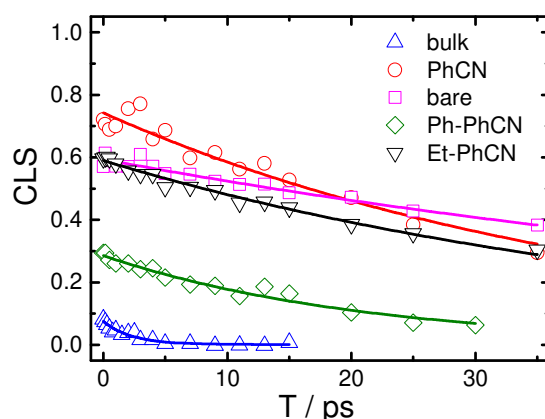


Figure 4. CLS dynamics of PhCN in bulk DEE (30 mM), MLs of PhCN on a 1 nm Au layer incubated in DEE (blue), as well as bare (magenta) as well as MMLs of Ph-PhCN and Et-PhCN incubated with DEE. Symbols represent experimental data while solid lines represent exponential fits as described in the text.

MMLs moreover allow for further disentangling of contributions to spectral diffusion. For instance, dilution of functional groups on the surface increases the mutual distance between the CN groups and thus results in less favourable condition for, *e.g.* excitonic coupling³¹ or excitation energy transfer^{6,32} (EET) between CN groups. The expectation is that the spectral diffusion gets slower in MMLs as compared to MLs if such contributions are eliminated from the underlying dynamics. The observation of even faster spectral diffusion (21 ps, green) in case of the Ph-PhCN MML as compared to the pure PhCN ML thus strongly speaks against occurring coupling or EET between the CN groups. This result is in agreement with conclusions previously drawn from spectral diffusion of immobilized aliphatic azide-containing MLs.¹⁸ Moreover, the acceleration of spectral diffusion of the MML system indicates that part of the underlying dynamics stem from electrostatic interaction of the CN groups with the solvent molecules. This is because MMLs allow for better exposure of the groups to solvent molecules as compared to a densely packed ML containing only PhCN molecules. Otherwise, intermolecular interactions of the aromatic systems in the PhCN ML and the Ph-PhCN MMLs are expected to be similar.

It is, however, interesting to note that this expectations is not always met for other kinds of MMLs. For instance, co-adsorption of PhCN with mercaptoethanol (Et) to form Et-PhCN MMLs (ratio 5:1) results in similar spectral diffusion dynamics (45 ps, black) as compared to pure PhCN ML. This most likely indicates that a mixture of the different aliphatic and aromatic molecules on the surface does not take place, likely due to strong π -stacking interaction of the aromatic rings: The two compounds rather form sub-domains within the MLs of the similar type independent of each other which results then in a comparable ML structures between the PhCN MLs and the PhCN subsystem in the MML. Spectral diffusion might consequently be used to quantify the miscibility of molecules during co-immobilization.

4. CONCLUDING REMARKS

The focus on this study was directed on spectral diffusion dynamics of local vibrational probes in the MLs and MMLs. Spectral diffusion allowed for the determination of ultrafast structural dynamics of the sample molecules, their interaction with the environment and composition of the MLs/MMLs under different conditions of co-adsorption. In this regard, absent contributions of EET to spectral diffusion in the investigated systems is astonishing since the distance between the investigated CN groups is expected to be fairly low (sub-nanometer), possibly due to π -stacking interaction of the aromatic rings. While similar conclusions have been drawn from previous studies of other sample molecules^{6,18}, interaction between functional groups was identified in aliphatic samples equipped with amide moieties on Au nanoparticles previously and has been interpreted as excitonic coupling between adjacent functional groups³¹. We conclude that such interactions are strongly dependent on the functional groups under study and in the MLs. Consequently, future investigations on other systems are required to help gaining a better understanding on how molecules interact at interfaces.

As furthermore demonstrated here, 2D ATR IR spectroscopy allows for the investigation of ultrafast dynamics with samples with sub-ML coverage of functional groups, even for local vibrational probes with low extinction coefficients ($< 200 \text{ M}^{-1} \text{ cm}^{-1}$). This demonstration is particularly important since it allows for studying more complex and larger systems in future investigations. In this context, ultrafast vibrational dynamics in membrane proteins, polymer films or at electrochemical interfaces can be envisioned which have up to now only been studied routinely with comparatively low temporal resolution (approximately nanoseconds).^{21,33}

In the context of low absorbing samples, possible signal enhancement effects gain significant attraction. In particular Au nanoparticles and roughened surfaces have been widely applied to obtain increased sensitivity in stationary as well as ultrafast spectroscopy.^{13,31} The origin of such signal enhancement effects stems from the excitation of surface plasmon resonances in the nanoparticles which allows for significantly higher electric field strengths at the surface compared to the incident beams.³⁴ Regarding the experiments presented here, similar contributions can be expected due to the presence of rough surfaces which are generally obtained from sputter-coating sample preparation.³⁵ The details of the particular surface enhancement encountered in 2D ATR IR spectroscopy are currently under investigation and will be published independently.

Overall, 2D ATR IR spectroscopy was demonstrated as a powerful tool for studying structural dynamics of molecules at interfaces. This was shown here by measuring time-resolved, multi-dimensional signals of self-assembled organic MLs of thin Au-coated substrates with sub-ML coverage of local vibrational probes. As such 2D ATR IR spectroscopy can be considered as a valuable alternative to widely applied time-resolved methods in surface science such as sum-frequency generation spectroscopy.

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